PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : B01D 69/02, 67/00

A1

(11) International Publication Number: WO 93/11861

(43) International Publication Date: 24 June 1993 (24.06.93)

(21) International Application Number: PCT/US92/09406

(22) International Filing Date: 3 November 1992 (03.11.92)

(30) Priority data:
804,294 9 December 1991 (09.12.91) US

(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

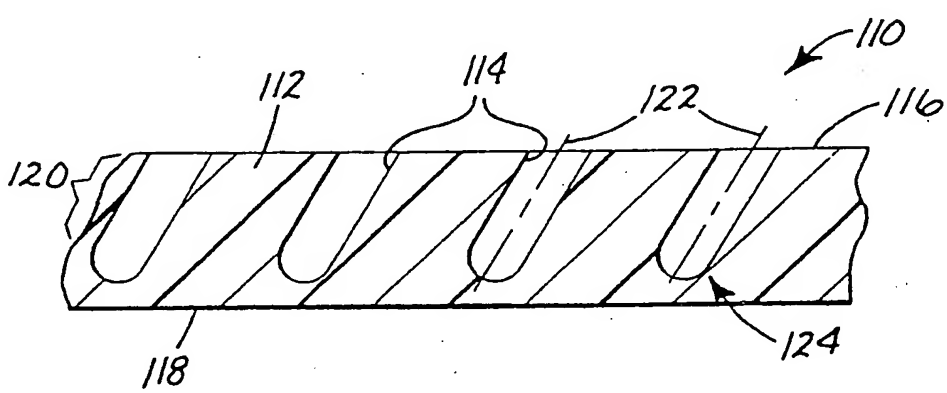
(72) Inventors: POURNOOR, Kaveh ; MOSHREFZADEH, Robert, S. ; McCLURE, Donald, J. ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: JORDAN, Robert, H. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).

Published
With international search report.

(54) Title: MICROSTRUCTURED MEMBRANES AND METHODS FOR MAKING SAME



(57) Abstract

Microstructured membrane comprising a sheet having first and second faces with an array of pores extending into the sheet from the first face, and in some instances extending through the entirety of the sheet. Substantially each pore within the array is individually surrounded by a flat land area and the major portion of the walls of each pore are substantially parallel to the longitudinal axis of the pore. The pores have an average characteristic dimension of between about 0.1 and about 5000 microns and a pore size distribution of less than about 10 percent, the longitudinal axes of pores within the array being substantially parallel with each other. Also, articles incorporating such membranes and methods for making such membranes.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Slovak Republic
CI	Côte d'Ivoire	KZ	Kazakhstan	SN	Senegal
CM	Cameroon	LI	Liechtenstein	SU	Soviet Union
CS	Czechoslovakia	LK	Sri Lanka	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MG	Madagascar	US	United States of America
ES	Spain	ML	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		

MICROSTRUCTURED MEMBRANES AND METHODS FOR MAKING SAME

Field of Invention

The present invention relates to microstructured membranes having arrays of defined pores therein, articles incorporating such membranes, and methods for making such membranes.

Background

Certain types of microstructured membranes with a plurality of cavities and orifices therein are known.

U.S. Patent No. 2,345,080 (Von Ardenne) discloses production of filters by perforating a foil with ion rays. U.S. Patent No. 3,303,085 (Price et al.) discloses formation of molecular sieves utilizing charged particle radiation. U.S. Patent No. 3,612,871 (Crawford et al.) discloses a method for treating plastic film by charged particle irradiation and then treatment with a selected solvent to leave substantially cylindrical holes in the film.

U.S. Patent No. 4,044,222 (Kestenbaum) discloses a method of forming tapered apertures in thin films.

U.S. Patent No. 4,092,515 (Joslin et al.) discloses a method of drilling a hole in a workpiece, the hole being substantially free of a recast layer, the method comprising laser irradiation of a workpiece in an oxidizing environment. U.S. Patent No. 4,262,186 (Provancher) discloses a process for forming holes in a substrate employing laser perforation of a chemical mask, chemical etching of the substrate through the perforated mask, and then removing the mask to yield the substrate with holes therein. U.S. Patent No. 4,855,049 (Toulemonde et al.) discloses formation of porous membranes by irradiation of a film from two sides with ionizing radiation and chemical etching.

U.S. Patent No. 4,652,412 (Chiulli) discloses a method for forming a microporous filter by embossing holes in an embossable polymer on a porous support.

Surface relief patterns and holes through films have been formed by methods utilizing laser irradiation. For instance, U.S. Patent No. 4,402,571 (Cowan et al.) discloses a method for producing a surface relief pattern utilizing laser interferometry. U.S. Patent No. 4,496,216 (Cowan) discloses formation of circular holes in photosensitive material utilizing exposure to at least three coherent beams of radiation.

U.S. Patent No. 4,923,608 (Flottman et al.) discloses membranes having tapered or rounded funnel-shaped pores with fixed pore size and a pore size distribution of less than 10 percent. The dividers between the pores are saddle-like and are of two different heights. The average pore diameters are said to range from 0.05 to 10 microns. The membranes are manufactured through erosion of pores using one or more intensity modulated laser beams projected onto a substrate.

U.S. Patent No. 4,032,743 (Erbach et al.) discloses a laser microperforator.

Summary of Invention

The present invention provides novel microstructured membranes having an array of pores therein, articles incorporating such membranes, and novel methods for making such membranes.

In brief summary, membranes of the invention comprise a sheet having first and second major faces with at least one array of pores that extend into the sheet from the first face. Depending upon the embodiment, the pores may be cavities that extend only partially through the sheet or the pores may be orifices that extend completely through the sheet, i.e., such that they open through both the first and

second major faces. At least 50 percent and preferably at least 75 percent of the length of the walls of each pore within a given array are straight. The land areas between pore openings are flat, i.e., divider portions between adjacent pores are of uniform height such that the distance between the first and second major faces is equal. In some embodiments, a major portion, i.e., at least 50 percent and preferably at least 75 percent of the length, of the walls of each pore within a given array are substantially parallel to the longitudinal axis of the pore. Typically, the pores have an average characteristic dimension of between about 0.1 and about 5000 microns and the pores within a given array are substantially uniform in size with a characteristic dimension distribution of about $\pm$ 10 percent or less about the average pore size. Also, the pores within a given array have substantially uniform orientation, with the longitudinal axes of the pores being substantially parallel, i.e., a deviation of less than about 5°, with each other.

Membranes of the invention differ from those previously available in a number of ways including but not limited to the following:

a) the pores within a given array can exhibit a degree of uniformity of size, shape, and/or orientation that was previously unattainable;
b) the pores can have desired shapes, sizes, and depth (i.e., in the case of cavities) and can be arranged in geometries not previously attainable;
c) the pores can be formed in membranes made of materials in which such pores could not previously be formed;
d) the membrane can exhibit a degree of side to side uniformity that was previously either not attainable or not readily attainable; and
e) the land areas between pore openings are flat.

As a result of their novel features, membranes of the invention provide unexpected and/or previously unattained advantages and utility.

Briefly summarizing, one novel method for making membranes of the invention comprises:

a) providing a mask with an array of apertures therein, the apertures being of the desired surface shape and size of the pores and being arranged in the pattern in which the pores are desired;

b) positioning the mask in close proximity, preferably in contact, with the first face of the film from which the membrane is to be made; and

c) forming an array of pores simultaneously in the film by application of directional means of boring through the mask, e.g., ablation or etching;

to yield a membrane with an array of pores therein.

Membranes of the invention may be used for a variety of purposes with advantageous results. For instance, they may be used as filter media, articles with microstructured surfaces, etc. Membranes of the invention may be substantially flat or may be non-planar as desired.

Brief Description of Drawing

The invention will be further explained with reference to the drawing, wherein:

Figure 1 is an illustration of a cross-section of a portion of one embodiment of a microstructured membrane with orifices of the invention;

Figure 2 is an illustration of a cross-section of a portion of another embodiment of a microstructured membrane with cavities of the invention;

Figure 3 is an illustration of a cross-section of a portion of another embodiment of a microstructured membrane of the invention;

Figure 4 is a scanning electron microscope photograph of the membrane fabricated in Example 1; and

Figures 5a-5d are a series of illustrations of a cross-section of a portion of a sheet during the process of making a membrane of the invention as described in Example 13.

These figures, which except for Figure 4 are idealized and not to scale, are intended to be merely illustrative and non-limiting.

Detailed Description of Illustrative Embodiments

Figure 1 shows an illustrative embodiment of a membrane of the invention wherein membrane 10 comprises sheet 12 with pores 14 therein. In the embodiment shown, pores 14 open in first face 16 of sheet 12 and extend through the entirety of sheet 12 to open through second face 18 also. Pores which extend through the entirety of the sheet are sometimes referred to herein as orifices.

Another illustrative embodiment is shown in Figure 2 wherein membrane 110 comprises sheet 112 and pores 114 that open in first face 116 of sheet 112 but extend through only a portion of sheet 112 and do not open through second face 118 thereof. Such pores are sometimes referred to herein as cavities. Membranes may be made with two or more arrays of cavities having varying depth if desired.

An additional feature of some embodiments is that, referring to Figure 2, major portion 120 of the walls of each opening 114 are substantially parallel to longitudinal axis 122 of opening 114. As used herein, "longitudinal axis" refers to the axis of the pore extending from the first face of the membrane into the sheet. The longitudinal axis of the openings in a membrane of the invention is generally parallel to the axis of application of the directional means for boring by which the openings are formed. By "substantially

parallel" it is meant that the deviation between the major portion of the wall of each opening and the longitudinal axis is less than about 5°. Accordingly, in these embodiments a pore has a substantially uniform cross-sectional area throughout at least the portion defined by the major portions of its walls. As used herein, "cross-sectional area" refers to the area of a geometric surface on a plane perpendicular to the longitudinal axis of the pore and bounded by the intersection of the plane with the walls of the opening.

In membranes of the invention, the major portion, i.e., at least 50 percent and typically preferably at least 75 percent, of the length of the walls of each pore beginning at the edge of the opening in the first face of the sheet and extending into the sheet are substantially straight. Explained in another way, the regions of intersection with the walls or sides of a pore of any plane parallel to and intersecting the longitudinal axis of the pore are straight lines for at least 50 percent and typically preferably at least 75 percent of the length of the regions of intersection beginning at the edge of the pore's opening in the first face of the sheet.

In the case of cavities, the second end of the pore, i.e., the end opposite the end that opens in the first face of the membrane is typically somewhat tapered or rounded. Referring to Figure 2, this second end is referred to herein as foot 124. Depending upon the characteristics of the means of boring employed and the characteristics of the film, the foot may exhibit string-like features or nodules, cones, or other irregularities sometimes referred to as artifacts. Dyer, Jenkins, and Sidhu, <u>Development And Origin Of Conical Structures On XeCl Laser Ablated Polyimide</u>, Applied Physics Lett., V. 49, Iss. 8, pp 453-55, 1986,

suggests that such artifacts may be due to impurities in the sheet from which the membrane is being made.

Membranes of the invention may be made with pores having an average "characteristic dimension" of desired size. As used herein, "characteristic dimension" means the largest cross-sectional dimension of the pore in a plane perpendicular to the longitudinal axis of the pore. Typically, the average characteristic dimension of pores in membranes of the invention is between about 0.1 and about 1000 microns. An advantage of the present invention is that the membrane may have, within a given array of pores, a pore size distribution at the first face of the sheet of less than about 10 percent and sometimes less than 5 percent. As used herein, "pore size distribution" means the standard deviation of the average characteristic dimension. Similar size distributions may be achieved for the openings on the second face of the sheet for orifices.

Membranes of the invention may be made with pores having a variety of shapes, i.e., cross-sectional profile of the pore as the region of a plane perpendicular to longitudinal axis of the pores bounded by the pore walls. For instance, by selection of a suitable mask, pores may have a cross-sectional profile that is circular, ovate, rectangular, triangular, some other polygon, or irregular shapes.

Membranes of the invention may be made with a desired density of pores. Typically, the first face of the membrane may have a surface porosity of at least about 0.01 percent, sometimes at least about 5 percent, and if desired at least about 20 percent or more. By selection of pore shape and orientation, membranes of the invention may be made with very high surface porosity, e.g., up to about 75 percent or even 95 percent. As used herein, "surface porosity" is the percentage of the area of the face of the membrane

where the film material has been bored away to yield the pores. It will be understood that as surface porosity increases, the structural strength of the resultant membrane decreases.

Membranes of the invention may be made from films of many types including polymeric materials, glass, ceramics, and metals. As discussed below, selection of the film material and selection of the boring means are dependent in part upon one another.

In general, ultraviolet boring techniques, e.g., ablation, may be used with polymeric films that contain unsaturated bonds. Membranes may be made using ultraviolet boring techniques with other polymers by incorporating ultraviolet absorbers therein to render the film ablative. Illustrative examples of polymeric film materials which may used to make membranes of the invention using ultraviolet ablative techniques include: polyvinyls such as acrylics and methacrylics, polyynes, polyenes (e.g., polyethylene, polypropylene, and polystyrene), polydienes (e.g., polybutadiene and polyisoprene), polyesters (e.g., terephthalate esters, etc.), polyurethanes, polyamides (e.g., nylons), polyimides, polyethers, etc. Some polymeric materials inherently exhibit sufficient ultraviolet absorption to be subject to ultraviolet-induced ablation. Ultraviolet sensitizing agents may need to be incorporated into other polymeric materials in order to render them sufficiently subject to ultraviolet-induced ablation. Such agents are well known and may be readily selected and used by those with ordinary skill in the art.

Ultraviolet ablation techniques may also be used to make membranes of the invention from sheets of some types of glass. Reactive ion etching techniques may be used to make membranes of the invention from sheets of some types of polymers, glass, ceramics, and metals.

Selection of the film material may also be made in light of the intended application of the membrane. For instance, many different nylons may be used where a relatively hydrophilic membrane is desired and polyethylene terephthalate may be used where a relatively hydrophobic membrane is desired.

Membranes of the invention may be made from rigid or flexible film materials as desired. For instance, polymeric membranes which can be wrapped around a 1 millimeter diameter mandrel without breaking can be made if desired.

An advantage of the present invention is that pores may be made in very thick films and in a variety of aspect ratios. Membranes of the invention may be made in a variety of thicknesses as desired, depending in many instances upon the application for which the membrane is being prepared. For example, membranes of the invention may be made from films having thicknesses of up to about 5000 microns. Also, membranes may be made with pores having very low aspect ratios, e.g., 1:100, or up to very high aspect ratios, e.g., 60:1. As used herein, "aspect ratio" refers to the ratio of (1) the interior length of the longitudinal axis of the pores, i.e., the portion of the longitudinal axis which is within the volume of film vacated during boring of the pores, to (2) the average characteristic dimension of the pores at the first face of the film.

An advantage of the highly uniform pore size and narrow distribution of pore size which can be achieved in membranes of the invention is that the resultant membranes can exhibit highly uniform characteristics. For instance, in the case of a membrane wherein the pores extend completely through the sheet, the membrane can be used as a filter which provides uniform separation properties across its entir ty. In such embodiments, where the pores have substantially uniform cross-sectional areas along their

full length, both sides of the membrane exhibit uniform properties. For example, filtration performance and flexural strength are substantially equal from either face of the membrane.

In some embodiments, membranes may be made wherein the walls of the pores define frustum-like shapes. In such instances, each pore does not have a uniform cross-sectional area and the major portions of the walls of each pore are not substantially parallel to the pore's longitudinal axis. Figure 3 illustrates membrane 210 comprising sheet 212 with pores 214 therein extending from first face 216 through second face 218. Major portions 220 of pores 214 are not parallel to each other or to longitudinal axis 222. For instance, pores may be made which have average characteristic dimensions at their largest end of between about 0.1 and about 5000 microns. As with other embodiments of the invention, however, at least 50 percent and preferably at least 75 percent of the length of the walls of each pore within a given array are straight. An advantage of such membranes is that they offer greater strength than do membranes with pores with similar minimum cross-sectional areas but having non-linear walls or wherein the dividers between adjacent pores are saddle-shaped. Some embodiments of such pores are sometimes referred to as being "Gaussian-shaped". Filter membranes with frustum-like orifices exhibit less tendency to clog when the stream being filtered enters the face of the membrane having the smaller ends of the orifices.

In some embodiments, membranes of the invention will comprise two or more arrays of different pores as described herein wherein the pores in different arrays have different characteristics. The arrays may be located at separate areas of the membrane or may be partially or totally superimposed.

An advantage of membranes of the invention is that the portions of the first face between pores, referred to herein as "land areas", and the land areas in the second face in those embodiments wherein the pores extend completely through the membrane, are substantially planar or flat. In comparison, the membranes disclosed in U.S. Patent No. 4,923,608 have saddle-like contours on the surface which would be subject to greater tendency to clog and exhibit more difficulty in backwashing and clearing than would filter membranes of the invention. In a tangential flow of fluid across either face of membranes of the invention, the lack of surface saddle-like structures will allow for a better sweep of the fluid across the surface and facilitate removal of filter cakes. Furthermore, membranes having saddle-like dividers between pores exhibit reduced flexural strength as compared to membranes of the invention.

In general, the methods for making membranes of the invention comprise:

a) providing a mask comprising a sheet with an array of apertures therein, the apertures being of the diameter and shape of the desired pores and being arranged in a pattern corresponding to that desired of the pores;

b) positioning the mask in close proximity to, preferably in intimate contact with, the first face of a film from which the membrane is to be formed; and

c) forming an array of pores simultaneously in the film by application of directional means for boring through the mask;

to yield the membrane with the array of pores therein.

Selection of means for boring will be based in part upon the nature of the mask used, the characteristics of the film from which the membrane is being made, and the features desired of the pores.

Illustrative examples of means for boring include application of a collimated stream of reactive ions, plasma, or collimated energy beam (e.g., excimer laser or ultraviolet beam). In addition to being highly directional, the means for boring is preferably one which substantially does not deform the sheet outside the area being bored, i.e., one which substantially causes only localized removal of sheet material in the desired location and not in the surrounding land areas. For this reason, conventional chemical etching is typically not desired for use in the present invention because it typically does not exhibit the desired directional boring. Preferably, by-products produced during boring, e.g., ablation by-products, are removed during boring such as by ventilation.

In some embodiments, the mask is placed in proximity, preferably in intimate contact, with the film after the mask is generated.

In other embodiments, the mask is generated from a precursor material in direct contact with the film. For instance, a mask may be generated by

a) applying a layer of resist material to the first face of the film from which a membrane is to be made;
b) imagewise exposing the layer of resist material with actinic radiation to differentially harden it;
c) removing the unhardened areas of the layer of resist material, exposing first areas of the first face of the film, the remaining, i.e., second areas of the first face remaining covered;
d) applying a cap coating to the exposed first areas of the first face and the remaining portions of the layer of resist material;
e) removing the remaining portions of the resist material and the cap coating thereon, thereby

exposing the second areas of the first face of the film.

The resist material can be imagewise exposed with a number of techniques, including selective scanning with a beam of suitable radiation, e.g., a laser beam of selected wavelength. In another technique, the imagewise exposure is performed with laser interferometry.

Examples

The invention will be further explained by the following illustrative examples which are intended to be nonlimiting.

In Examples 1 and 4 image analysis was performed utilizing an IBAS Image Analyzer with a 10X objective, 6.3X ocular, and green light filter to characterize the structure of the membrane and its constituent elements. All area ("Area"), diagonal ("D_{diag}"), and edge ("D_{edge}") dimension measurements were determined using the darkest continuous line of the aperture image. Area measurements were based on standard area determination criteria common to image analysis equipment and software. Diagonal and edge image dimension measurements were obtained by commonly utilized feret or caliper measurement techniques. Results for Area, D_{diag}, and D_{edge} determinations along with the calculated D_{diag}/D_{edge} ratio, referred to herein as the shape factor, which should be 1.4142 for a perfect square where D_{diag} is the diagonal of the square, and D_{edge} is the edge length for a square having the same area as the measured area, for the incident (Sample I) and exit (Sample E) membrane surface images was determined as shown below. In Example 13 the same device was used to determine the average diameter of the orifices formed.

Example 1

A stainless steel mask with uniformly distributed square apertures was placed in contact with a 12.2 micron (0.48 mil) thick poly(ethylene terephthalate) (i.e., "PET"), MYLAR™ film (from E.I. duPont de Nemours). The sides of the apertures were 53 microns in length with, according to the manufacturer, a standard deviation of about 10 percent and about 35 percent of the mask was open area.

The beam from a krypton/fluorine ("KrF") excimer laser producing 249 nanometer ("nm") radiation at a pulse frequency of 40 Hertz ("Hz") and pulse duration of 27 nanoseconds was projected through an iris and a series of lenses onto the mask. The iris was located about 30.5 centimeters ("cm") from the laser window and a few cm from the first lens. Three lenses from ESCO Products Company and made of CORNING™ 7490-UV, a material transparent to light at a wavelength of 249 nm, with AR-MgF_2 antireflective coatings including (1) a 106.7 cm focal length converging lens located about 108 cm (42.5 inches) from the PET film plane, (2) a 20.3 cm focal length diverging lens located about 73 cm (28 3/4 inches) from the PET film plane, and (3) a 3.4 cm focal length cylindrical lens located about 4 cm (1.5 inches) from the film plane were used.

Ablation was accomplished by shadowing the mask pattern onto the PET film. The intensity of the laser radiation incident to the surface of the film was about 200 millijoules per centimeter^2 ("mJ/cm^2") with a beam shape at the surface of a rectangle about 3 millimeters (120 mils) wide and 15.2 cm (6 inches) long. The mask and PET film were moved in register across the middle 10.2 cm (4 inches) of the beam at a rate of about 0.25 cm/minute.

Scanning the mask/film combination yielded a 10.2 cm wide PET membrane with pores penetrating

through the membrane. The axes of these pores were parallel to one another and perpendicular to the membrane surfaces. The sides of the openings of the square pores on the face of the sheet to which the laser was incident had an average length of 51.1 microns with a standard deviation of about 4 percent and the sides of the opening at the opposite face had an average length of 52.1 microns with a standard deviation of about 4 percent as determined by image analysis. Results for Area D_{diag}, and D_{edge} determinations (with standard deviation in parentheses) was as follows:

Sample	Area micron^2	D_{diag} microns	D_{edge} microns	Shape Factor	D_{area} microns
I	2459	67.8 (2.4)	51.1 (2.0)	1.326	49.6 (1.4)
E	2594	69.4 (2.1)	52.1 (1.9)	1.332	50.9 (1.4)

Within the absolute deviation of ± 2.0 microns for D_{diag} and ± 1.9 microns for D_{edge}, orifice dimensions on the incident and exit faces of the membrane are considered statistically identical.

Thus the sizes of either end of the replicated pores were the same within the statistical distribution of these dimensions. The sizes of the replicated pores were also within the statistical distribution of sizes of the apertures in the mask.

Example 2

A membrane was prepared as in Example 1 except a nickel mask having 5 micron diameter round apertures having a standard deviation of 10 percent and 0.2 percent open area (from PA Technologies) was substituted for the stainless steel mask.

A membrane having an array of 5 micron wide round pores was produced by exposure to a 500 mJ laser output at 45 Hz.

Example 3

A membrane was prepared as in Example 1 except the mask contained square apertures 20 microns wide having a standard deviation of 10 percent and had an open area of about 35 percent.

A membrane having an array of square pores with 20 micron sides was produced upon exposure to a 500 mJ laser output at 30 Hz.

Example 4

A membrane was prepared as in Example 1 except the mask contained square apertures 106 micron wide having a standard deviation of 10 percent with a square cross section and an open area of about 35 percent.

A membrane having an array of 106 micron pores was produced by exposure to a 500 mJ laser output at 45 Hz. Results for Area, D_{diag}, and D_{edge} determinations along with the calculated Shape Factor, and D_{area} for the incident (Sample I) and exit (Sample E) membrane surface images was as follows:

Sample	Area micron^2	D_{diag} microns	D_{edge} microns	Shape Factor	D_{area} microns
I	10722	144.0 (3.2)	104.8 (3.2)	1.375	103.5 (2.2)
E	10426	143.5 (3.5)	102.8 (3.6)	1.397	102.1 (2.4)

Within the absolute deviation of ± 3.2 microns for D_{diag} and ± 3.5 microns for D_{edge}, orifice dimensions on the incident and exit faces of the membrane are considered statistically identical.

Example 5

A membrane was prepared as in Example 4 except the PET film employed was about 102 microns thick.

A membrane having an array of 106 micron pores was produced by exposure to a 500 mJ laser output at 50 Hz.

Example 6

A membrane was prepared as in Example 1 except a 102 micron PET film was substituted for the 12.2 micron (0.48 mil) film.

A membrane having an array of regularly spaced square cavities 53 microns wide and having a depth of about 40 microns was produced by exposure to a 450 mJ laser output at 8 Hz.

Example 7

A sample was prepared as in Example 4 except a 102 micron PET film was substituted for the 12.2 micron film.

A membrane having an array of regularly spaced square cavities 106 microns wide and having a depth of about 40 microns was produced by exposure to a 500 mJ laser output at 8 Hz.

Example 8

A membrane was prepared as in Example 1 except a 102 micron PET film was substituted for the 12.2 micron film and a mask containing 212 micron apertures having a standard deviation of 10 percent with a square cross section and an open area of about 35 percent was substituted for the 53 micron mask.

A membrane having an array of regularly spaced square cavities 212 microns wide and having a depth of about 40 microns was produced by exposure to a 500 mJ laser output at 10 Hz.

Example 9

A membrane was prepared as in Example 1 except a 178 micron PET film was substituted for the 12.2 micron film.

A membrane having an array of regularly spaced square cavities 53 microns wide and having a depth of

about 100 microns was produced by exposure to a 450 mJ laser output at 21 Hz.

Example 10

A membrane was prepared as in Example 4 except a 356 micron PET film was substituted for the 12.2 micron film.

A membrane having an array of regularly spaced square cavities 106 microns wide and having a depth of about 300 microns was produced by exposure to a 500 mJ laser output at 50 Hz.

Example 11

A membrane was prepared as in Example 1 except a 50.8 micron KAPTON™ polyimide film (from duPont) was substituted for the PET film.

A membrane having a regularly spaced array of 53 micron square pores was produced by exposure to a 500 mJ laser output at 35 Hz.

Example 12

A membrane was prepared as in Example 1 except a 15.24 micron DARTEK™ Nylon 66 film (from duPont) was substituted for the PET film.

A membrane having an array of regularly spaced 53 micron square pores was produced by exposure to a 460 mJ laser output at 34 Hz.

Example 13

A 5 micron thick biaxially-oriented PET film having a surface roughness of 0.1 micron or less was clamped between a pair of flat frame members, each member having a circular opening of approximately 2 cm, with one member fitted with a circular rubber gasket to facilitate securing the film between the frame members. The PET film was then stretched by positioning the circular opening of the frame members over a beveled

cylinder having a diameter slightly smaller than the opening and applying uniform radial pressure to the assembly. A flat circular copper gasket was adhered to the stretched film using a UV curable adhesive (NORLAND™ 61 Epoxy from Norland Co.). After curing the adhesive, the film/gasket construction was removed from the frame assembly by cutting the film along the outside perimeter of the gasket.

The PET film was cleaned by immersing the film/gasket construction in a series of three ultrasonic cleaning baths (about 15 minutes in each bath) including an 0.1 percent aqueous detergent solution (LIQUI-NOX™ soap from Alconox, Inc.), acetone and isopropyl alcohol ("IPA"). The film was rinsed with ultrapure water, generated by passing tap water through a Barnstead "NANOpure™ II" water purification unit (from Barnstead, a division of Sybron Corp.) for 15 minutes after each bath. After the final rinse with ultrapure water the film was dried in a stream of pure nitrogen. Subsequent processing of the film to produce the porous membrane is illustrated in Figures 5a-5d.

A 0.6 micron thick positive photoresist coating (1400-17 SHIPLEY™ from Shipley), was applied to the clean, dry film in a spin coater apparatus and a pattern developed on the resist coating through two exposures to laser irradiation. The apparatus, which utilized Lloyd's mirror fringes phenomena (discussed by X. Mai, R. S. Moshrefzadeh, U. J. Gibson, G. I. Stegeman and C. T. Seaton in "Simple Versatile Method for Fabricating Guided-Wave Gratings," Applied Optics, vol. 24, No. 19, 1985), was equipped with a helium/cadmium ("HeCd") laser (from Liconix) operating at 442 nm, an electronic shutter to control exposure time, a spatial filter (from Jodon) which filtered out the high frequency components of the beam and collimated the beam to the desired size, and a sample/mirror assembly comprising a flat mirror

configured at 90° to the sample holder. The mirror had a flatness of lambda/40.

The resist-coated film/gasket assembly was mounted on the sample holder such that half of the incident laser beam illuminated the resist coating directly and the other half of the beam was reflected onto the coating by the mirror. An interference between the two portions of the beam created a periodic interference pattern in the resist coating. Periodicity of the pattern was controlled by adjusting the angle alpha between the mirror and the incident beam. The period was calculated using the formula:

P = lambda/(2 sine alpha)

where P is the eventual pore period and lambda is the laser wavelength (442 nm). Prior to the second exposure, the resist coated film was rotated 90° on the sample holder.

Figure 5a illustrates film 312 with resist coating 330 thereon. Following exposure, resist coating 330 has unexposed areas 332 and exposed areas 334.

After the second exposure, the resist layer was developed for 30 seconds in a 1:4 solution of SHIPLEY™ Developer 351 (from Shipley) in ultrapure water to remove unexposed resist. The resulting developed structure consisted of an array of regularly spaced posts 332 of hardened resist coating on the film. A 0.1 micron thick titanium ("Ti") coating was vapor coated onto the developed structure in a vacuum chamber using Ti vapor and directional coating techniques. Divergence of the coating beam was approximately 10° and the film was placed approximately 100 cm from the Ti boat. Figure 5b illustrates the resultant intermediate of film 312 with unexposed posts 332 of the resist coating and titanium coating 336 thereon. The intermediate was then placed in an ultrasonic bath containing acetone for a few minutes to dissolve the

posts, leaving the underlying areas of the film exposed.

Directional etching of the film using reactive ion etching ("RIE") with oxygen for two hours at 200 watts and an oxygen pressure of about 30 millitorrs followed by chemical wet etching with a mixture of 50 parts by volume of a 5 weight percent aqueous solution of ethylenediamine tetraacetic acid ("EDTA"), 4 parts by volume of ammonium hydroxide, and 10 parts by volume of a 30 weight percent aqueous solution of hydrogen peroxide to remove the Ti mask yielded a microporous membrane. Figure 5c illustrates application of RIE beam 338 to the exposed areas of film 312 with the remaining portions of titanium coating 336 serving as a mask. Figure 5d illustrates membrane 310 with pores 314 following completion of RIE and removal of the titanium mask. Image analysis of the resultant membrane indicated the orifices had an average characteristic dimension of 0.7058 ± 0.0794 microns.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

Claims:

1. A microstructured membrane comprising a sheet having a first major face and a second major face with an array of pores extending into said sheet from said first face characterized in that substantially each pore within said array is individually surrounded by a flat land area, said pores having an average characteristic dimension of between about 0.1 and about 5000 microns and a pore size distribution of less than about 10 percent, the longitudinal axes of said pores being substantially parallel with each other.

2. The membrane of claim 1 further characterized in at least one of the following:
  a) said sheet comprises one or more of the following: glass, ceramic, metal, or polymer; or
  b) said sheet is made of a material that is subject to directional ablation by exposure to ablative radiation or reactive ion etching; or
  c) said sheet comprises one or more of the following: polyvinyls, polyynes, polyenes, polydienes, polyesters, polyurethanes, polyamides, polyimides, polyethers, and polycarbonates.

3. The membrane of claim 1 further characterized in at least one of the following:
  a) said sheet is less than about 50 microns thick; or
  b) said sheet has a thickness greater than about 50 microns; or
  c) said sheet has a thickness up to about 5000 microns.

4. The membrane of claim 1 further characterized in at least one of the following:
  a) the longitudinal axis of said pores is substantially perpendicular to said first face; or

b) the longitudinal axes of substantially all of said pores are substantially parallel.

5. The membrane of claim 1 further characterized in at least one of the following:

a) each face has substantially flat land areas; or

b) said first face has a surface porosity of at least about 5 percent; or

c) said first face has a surface porosity of at least about 20 percent; or

d) said first face has a surface porosity of at least about 40 percent.

6. The membrane of claim 1 further characterized in at least one of the following:

a) the major portion of the walls of each said pore are substantially parallel to the longitudinal axis of said pore; or

b) at least 50 percent of the length of the walls of said pores are parallel to the longitudinal axis of the pores; or

c) at least 75 percent of the length of the walls of said pores are parallel to the longitudinal axis of the pores; or

d) the cross-sectional areas of said pores are substantially uniform throughout at least 50 percent of the length of the longitudinal axes of said pores; or

e) the cross-sectional areas of said pores are substantially uniform throughout at least 75 percent of said longitudinal axes; or

f) at least 50 percent of the length of the walls of said pores are straight; or

g) at least 75 percent of the length of the walls of said pores are straight.

7. The membrane of claim 1 further characterized in that said pores extend completely

through said sheet from said first face to said second face and the burst resistance of said membrane is isotropic.

8. The membrane of claim 1 further characterized in at least one of the following:

a) said pores have a pore size distribution of less than about 10 percent.
b) the area of opening and spatial arrangement of said pores is substantially uniform across said first face; or
c) said pores extend completely through said sheet from said first face to said second face wherein and the cross-sectional areas of said pores are substantially uniform throughout at least 50 percent of the length of the longitudinal axes of said pores.

9. The membrane of claim 1 further characterized in that said membrane further comprises at least a second array of pores extending into said sheet from said first face wherein substantially each pore within said second array is individually surrounded by a flat land area and the major portion of the walls of each said pore are substantially parallel to the longitudinal axis of said pore, said pores having an average characteristic dimension of between about 0.1 and about 5000 microns and a pore size distribution of less than about 10 percent, the longitudinal axes of said pores within said array being substantially parallel with each other;

wherein (1) at least one of said average characteristic dimension, said pore size distribution, depth, or shape of the pores of said second array is different from said average characteristic dimension, said pore size distribution, depth, or shape of the pores of said first array; and/or (2) said longitudinal axes of the pores of said second array is at least 5°

different from said longitudinal axes of the pores of said first array.

10. A membrane comprising a sheet having first and second faces with pores extending into at least said first face characterized in that the walls of each said pore form a frustum-like shape, said pores having an average characteristic dimension at their largest end of between about 0.1 and about 5000 microns and a pore size distribution at their largest end of less than about 10 percent, the central axes of said pores being substantially parallel.

11. A method for making a membrane of claim 1, characterized in that said method comprises:

a) providing a mask comprising a sheet with an array of apertures therein, said apertures being of the desired shape and characteristic dimension of said pores and being arranged in the pattern in which said pores are desired;
b) positioning said mask in close proximity with the first face of a film having two faces; and
c) forming an array of pores simultaneously in said film by application of directional means for boring through said mask;

to yield said membrane.

12. The method of claim 11 further characterized in that said boring comprises application of a collimated stream of reactive ions or collimated energy beam through said mask.

13. The method of claim 11 further characterized in that said mask is generated while said sheet is in direct contact with said film.

14. The method of claim 13 further characterized in that said mask is generated by:

a) applying a layer of resist material to said first face of said film;

b) imagewise exposing said layer of resist material with actinic radiation to differentially harden said resist material;

c) removing the unhardened areas of said layer of resist material, exposing first areas of said first face of said film;

d) applying a cap coating to said exposed areas of said first face of said film and the remaining portions of said layer of resist material; and

e) removing the remaining portions of said resist material and the cap coating thereon, thereby exposing second areas of said first face.

15. The method of claim 11 further characterized in that said imagewise exposing is performed with laser interferometry.

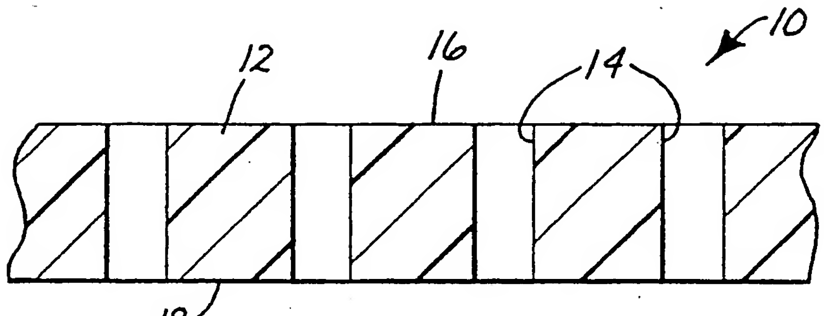


Fig 1

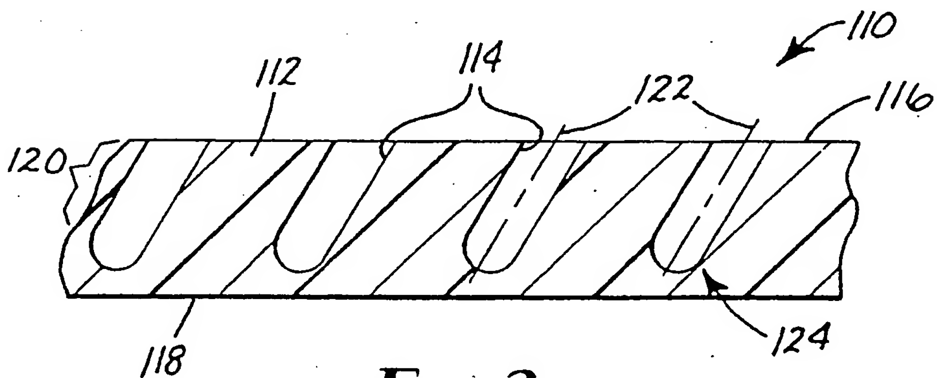


Fig 2

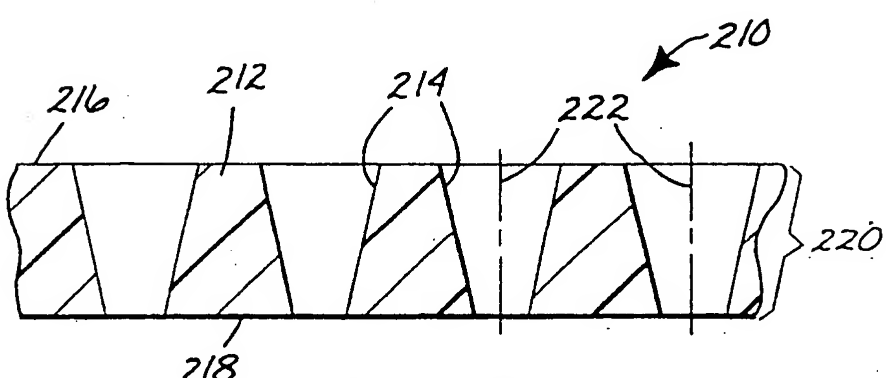


Fig. 3

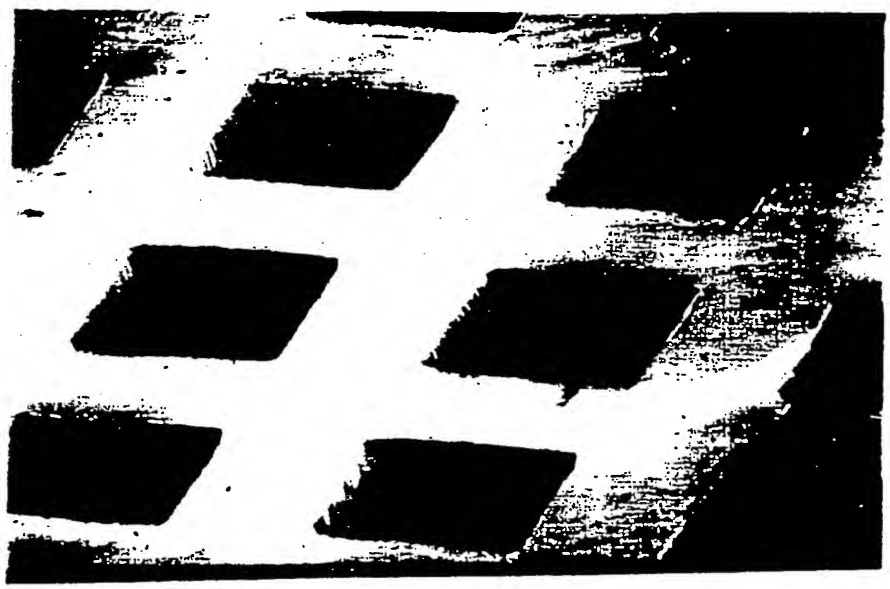


Fig. 4

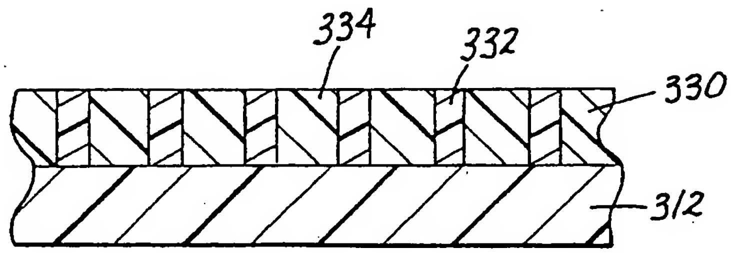


Fig. 5A

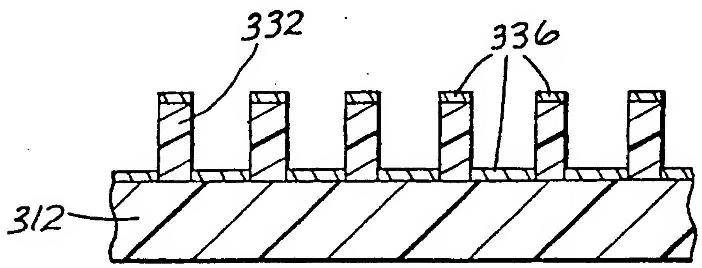


Fig. 5B

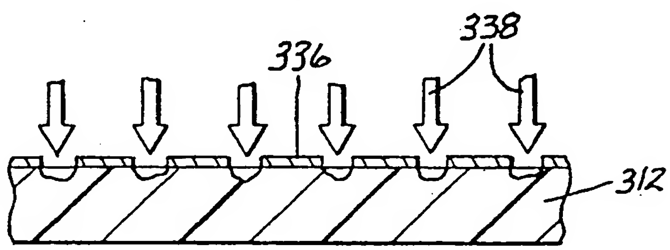


Fig 5C

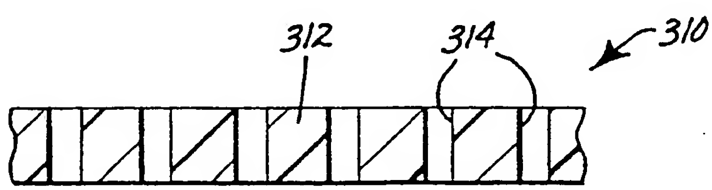


Fig. 5D

INTERNATIONAL SEARCH REPORT

rnational application No.

PCT/US 92/09406

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01D 69/02, B01D 67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0459893 (CYCLOPORE S.A.), 4 December 1991 (04.12.91) --	1-15
A	US, A, 4923608 (T. FLOTTMANN ET AL), 8 May 1990 (08.05.90) -- --------	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 February 1993	12.03.93

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Britt-Marie Lundell

INTERNATIONAL SEARCH REPORT
Information on patent family members

29/01/93

International application No.
PCT/US 92/09406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0459893	04/12/91	CA-A- 2043624	02/12/91
		FR-A- 2662635	06/12/91
US-A- 4923608	08/05/90	DE-A- 3742770	29/06/89
		EP-A- 0325752	02/08/89
		JP-A- 2043927	14/02/90